



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Selective Precipitation of Rare Earth Chlorides from LiCl-KCl

*Michael F. Simpson and Tae-Sic Yoo
Idaho National Laboratory*

*Michael Shaltry and Supathorn Phongikaroon
University of Idaho*

*Daniel LaBrier and Michael Lineberry
Idaho State University*

*2012 International Pyroprocessing Research
Conference
Fontana, Wisconsin
August 26-29, 2012*



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

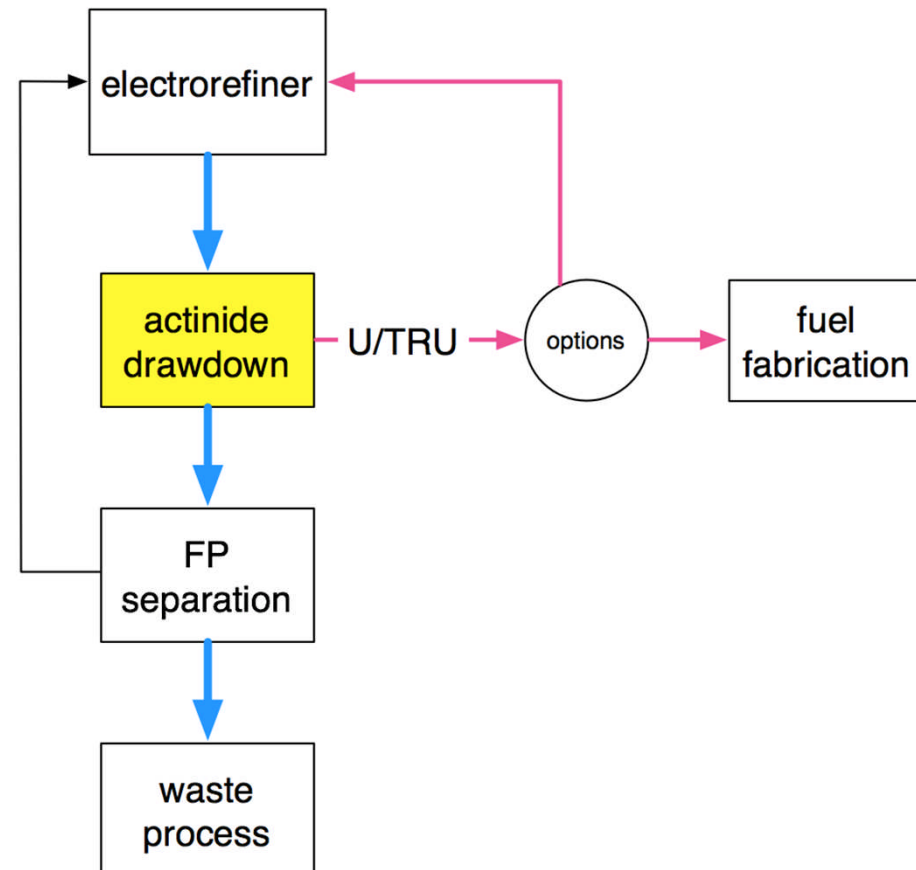
Actinide Drawdown as Key Component of ER Salt Waste Treatment

■ Fuel processing objectives

- Recover high % of actinides
- Minimize high level waste
- Minimize processing cost
- Support safeguards objectives

■ Actinide drawdown unit operation functions

- Remove high % of actinides from salt to prevent their loss into the waste process
- Recover actinides in form suitable for recycle to the ER or use in new fuel fabrication
- Produce salt suitable for processing in the FP separation unit operation or direct into the waste process





Options for Achieving Drawdown

■ Electrolysis

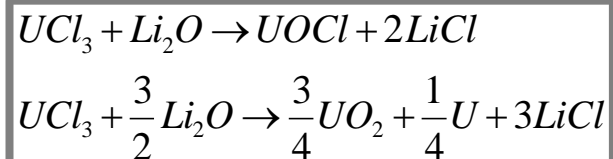
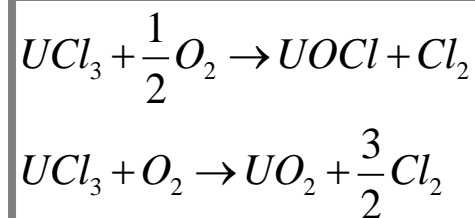
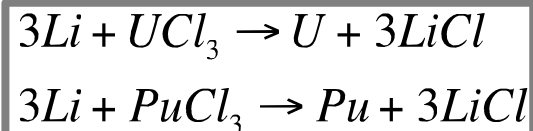
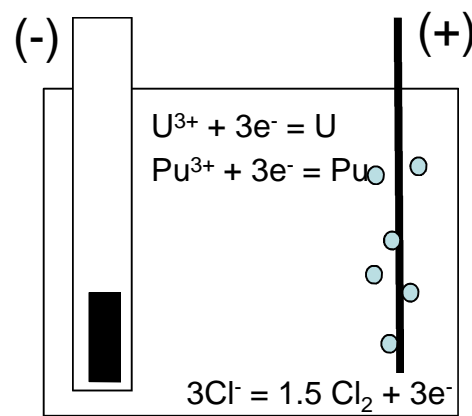
- Results in chlorine gas evolution
- Difficult to drive high extent of actinide removal due to concentration overpotentials

■ Chemical Reduction

- Reduction via metals such as Li and K
- Selectivity and product recovery viewed as challenges
- But scale up potential appears to be excellent

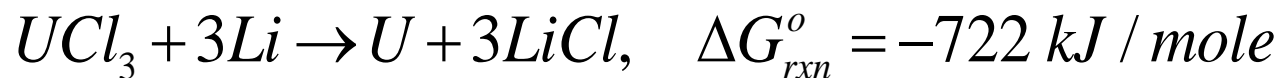
■ Chemical oxide formation

- O₂ gas bubbling
- Addition of Li₂O to molten salt
- Selectivity and product recovery viewed as challenges
- Also appears to be suitable for scale-up

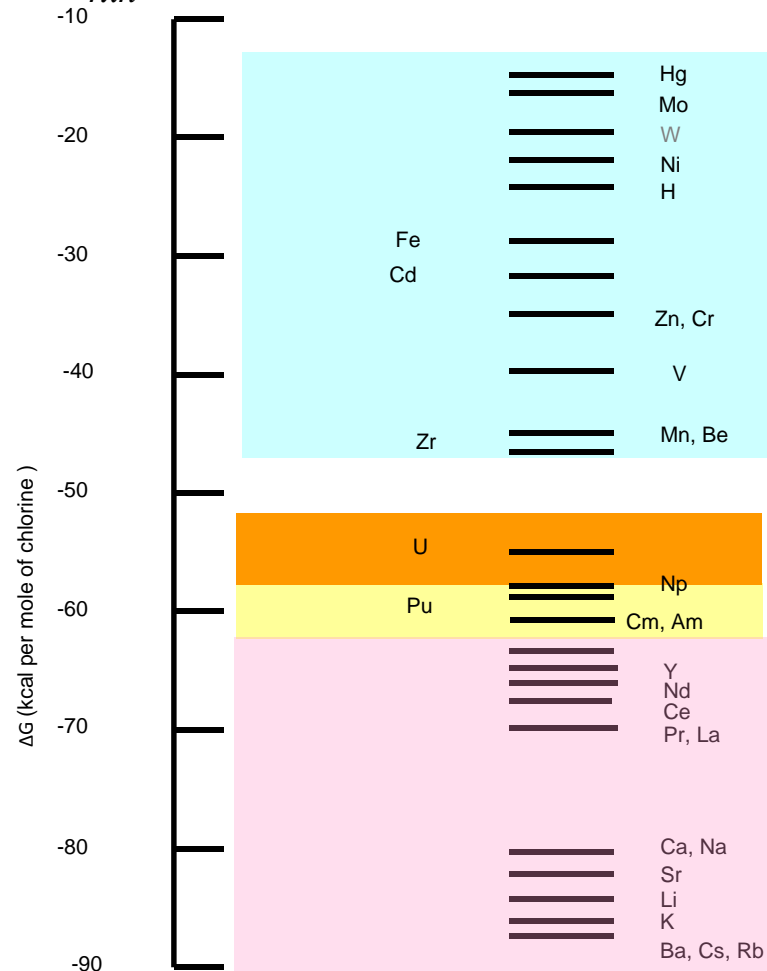




Metal Precipitation from Li Reduction



- Simple process known to work for reducing UCl_3 concentration to prepare for U/TRU recovery using a liquid cadmium cathode
- More readily scaled up than electrolytic processes (not constrained by electrode current densities)
- Free energy of formation values appear to be favorable with respect to being able to separate actinides from rare earths.
- Experimental study needed due to uncertainty associated with non-ideal characteristics of the molten salt/metal systems.
- Initial experimental studies used only selectivity relative to different rare earths for simplicity and cost effectiveness.





U.S. DEPARTMENT OF
ENERGY

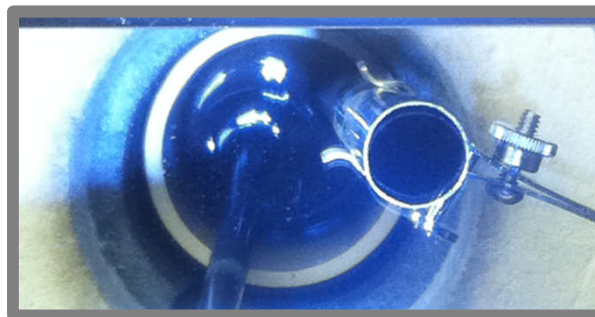
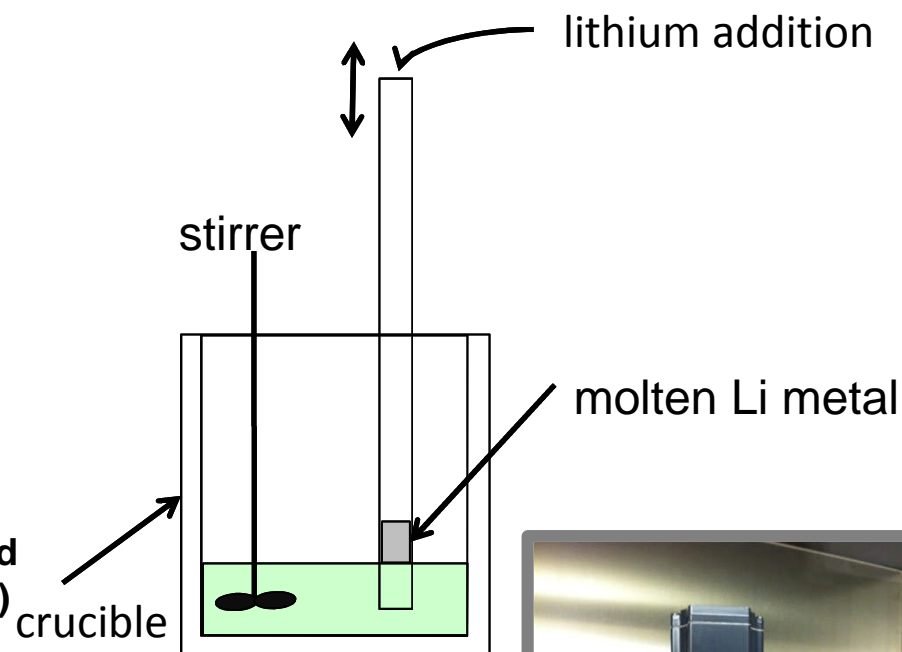
Nuclear Energy

Experimental Design for Rare Earth Reduction with Lithium

Experimental Procedure

1. MgO crucible and salts loaded into inert atmosphere glove box (Ar w/ <10 ppm H_2O & O_2)
2. Quaternary salts ($\text{LiCl-KCl-XCl}_x\text{-MCl}_y$) heated to 500 C for ~12 hrs prior to each test
3. Stirrer rotated at 60 rpm
4. Lithium added to tube inserted in the salt (see diagram)
5. Salt samples taken every 2-4 hrs and analyzed via ICP-MS (stirring stopped during sampling)

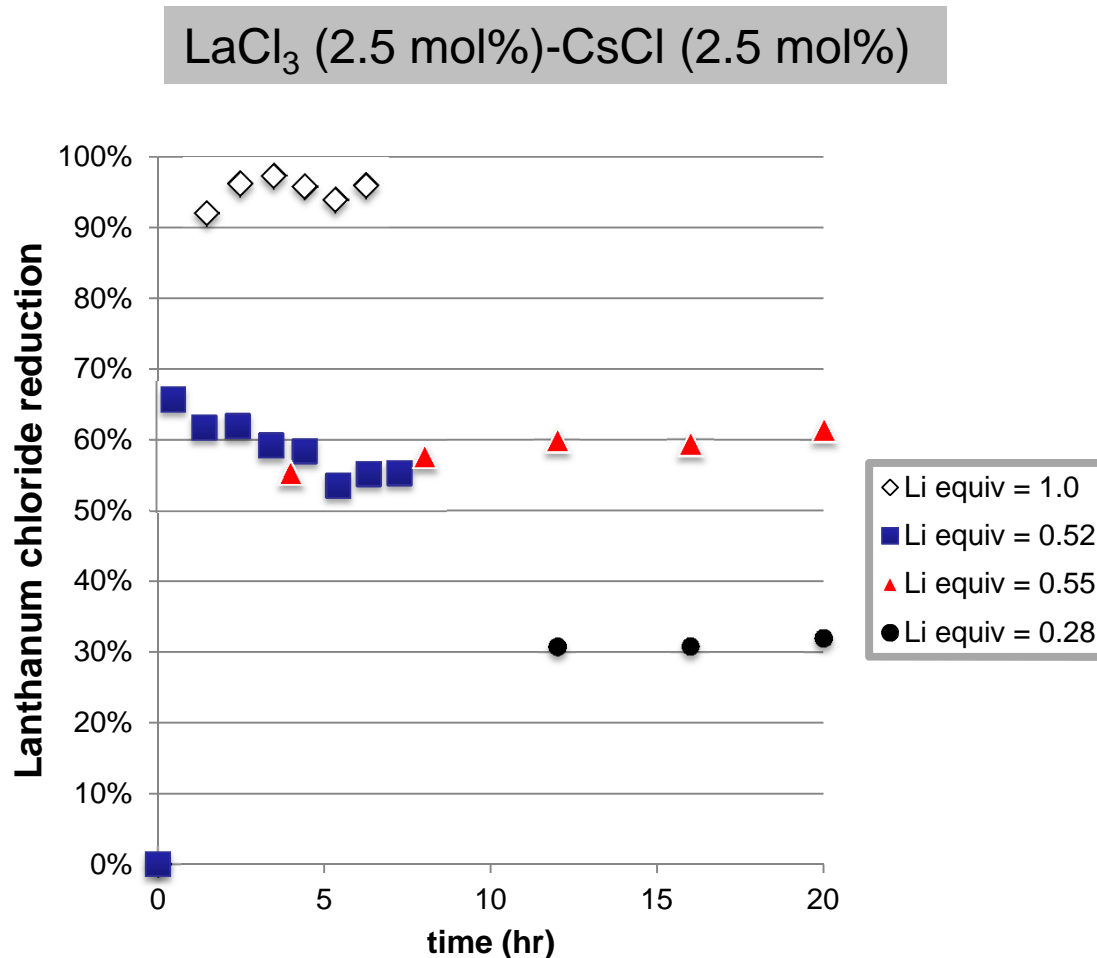
Objective was to measure selectivity and reaction kinetics and understand process limitations. Rare earths used as surrogates for actinide/rare earth mixtures.





Kinetics of Lithium Reduction

- Equilibrium was typically reached in under 10 hrs
- Concentration drift observed in some experiments
 - Attributed to poor glove box atmosphere in early experiments
- Complete lithium consumption evidenced by mole equivalents reacted divided by moles of lithium added typically in the range of 1.0 to 1.2.

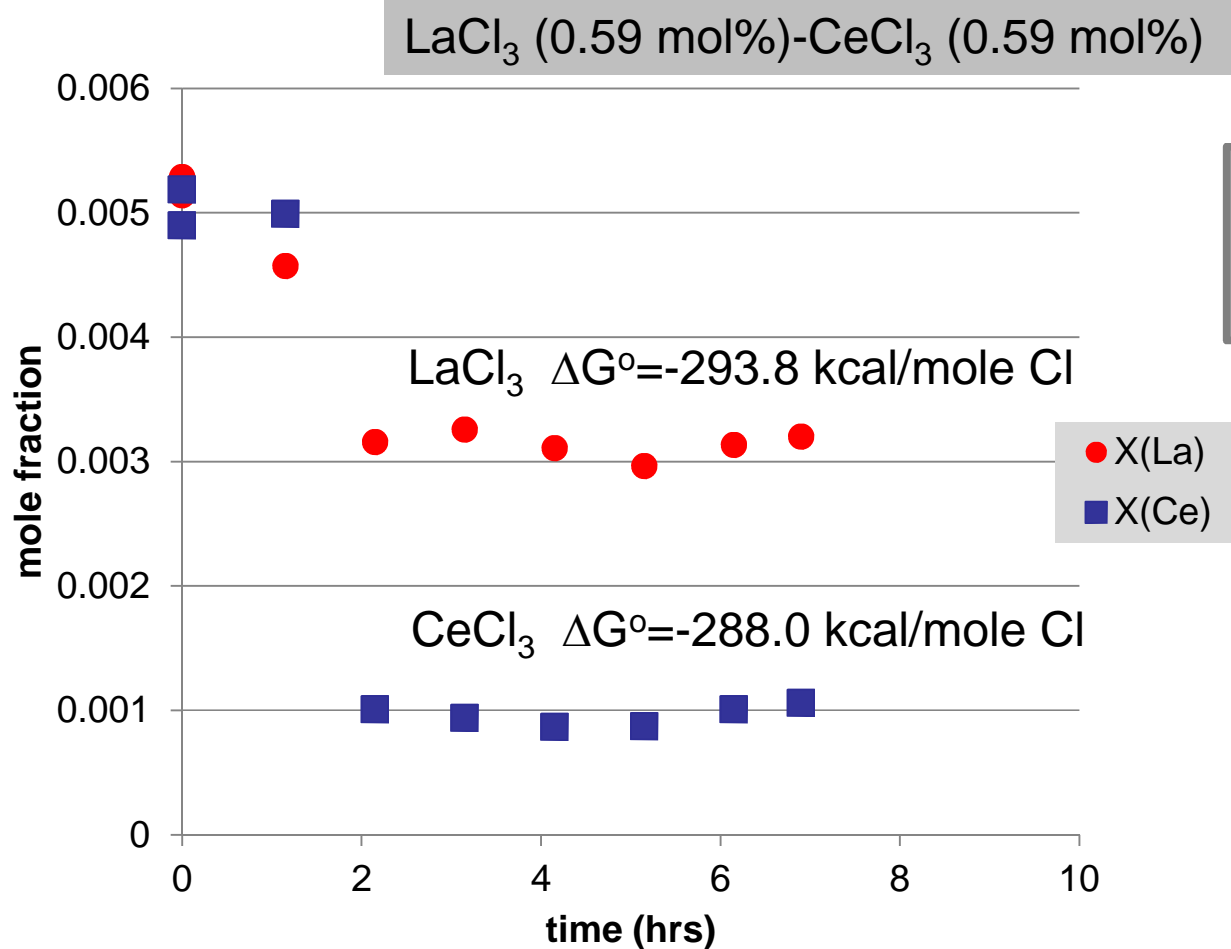




U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Simultaneous Reduction of Different Rare Earth Chlorides



Note- only salt sampled.
metal precipitate observed
but not sampled.



Post drawdown salt showing
Metal deposit layer



Lithium Drawdown Model

- Assume lithium completely reacts with the most reactive of the two rare earth chlorides. Extra Li then reacts with the other rare earth chloride.
- Then equilibrium is assumed to be established by reaction of the metals and metal chlorides such as in the case of La and Ce.



- A simple equilibrium expression can be derived.

$$K' = \frac{x_{Ce}^{EQ} y_{La}^{EQ}}{x_{La}^{EQ} y_{Ce}^{EQ}}$$

x=mole fraction in salt
y=mole fraction in metal

- K' can be expressed in terms of fundamental properties. But the activity coefficients are not known. So, the lumped parameter can be determined via fit to data

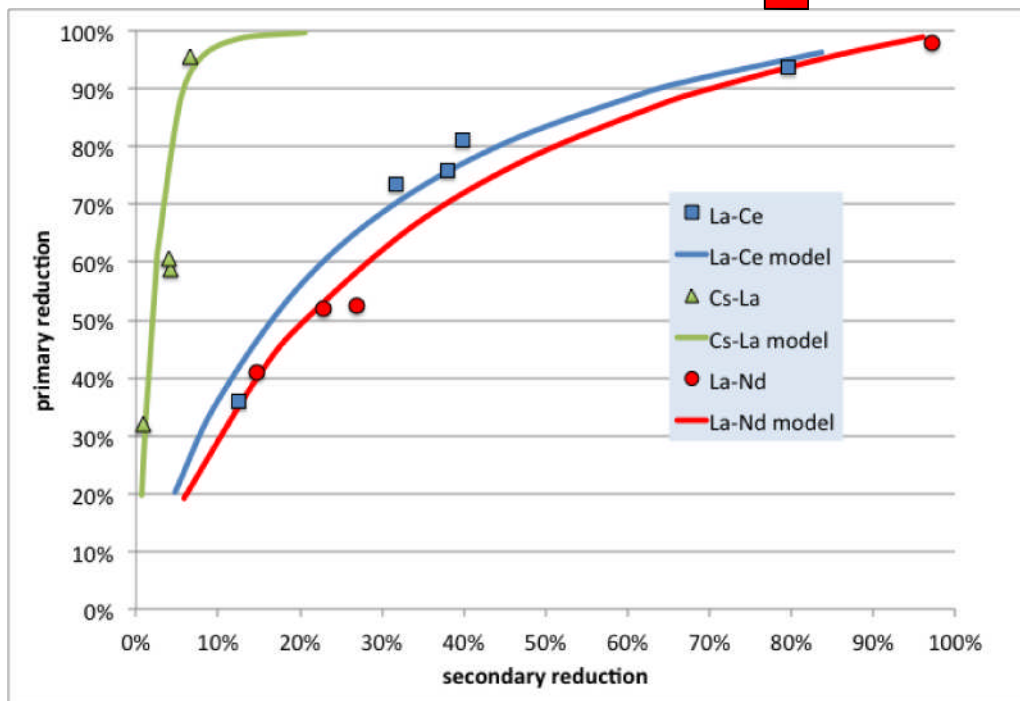
$$K' = \frac{\gamma_{LaCl_3} \gamma_{Ce}}{\gamma_{La} \gamma_{CeCl_3}} e^{-\frac{\Delta G^o}{RT}}$$



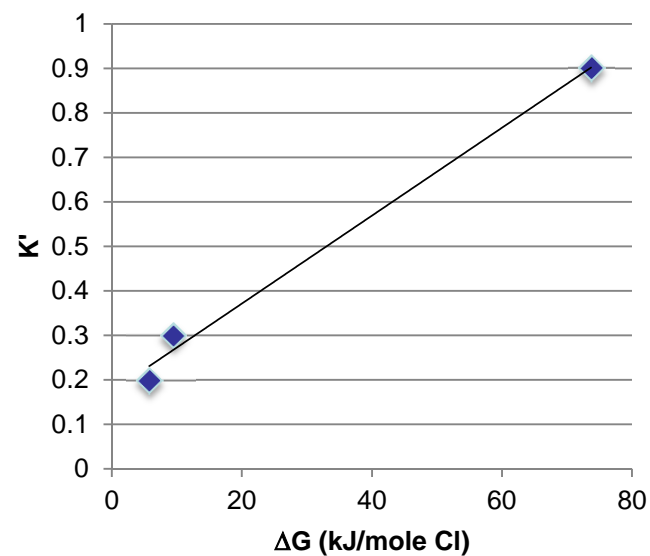
U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Comparison of Equilibrium Results to Model



Primary Species	Secondary Species	K' (fit)	ΔG (kJ/mol Cl)
LaCl ₃	CsCl	0.9	73.7
CeCl ₃	LaCl ₃	0.2	5.8
NdCl ₃	LaCl ₃	0.3	9.4





U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

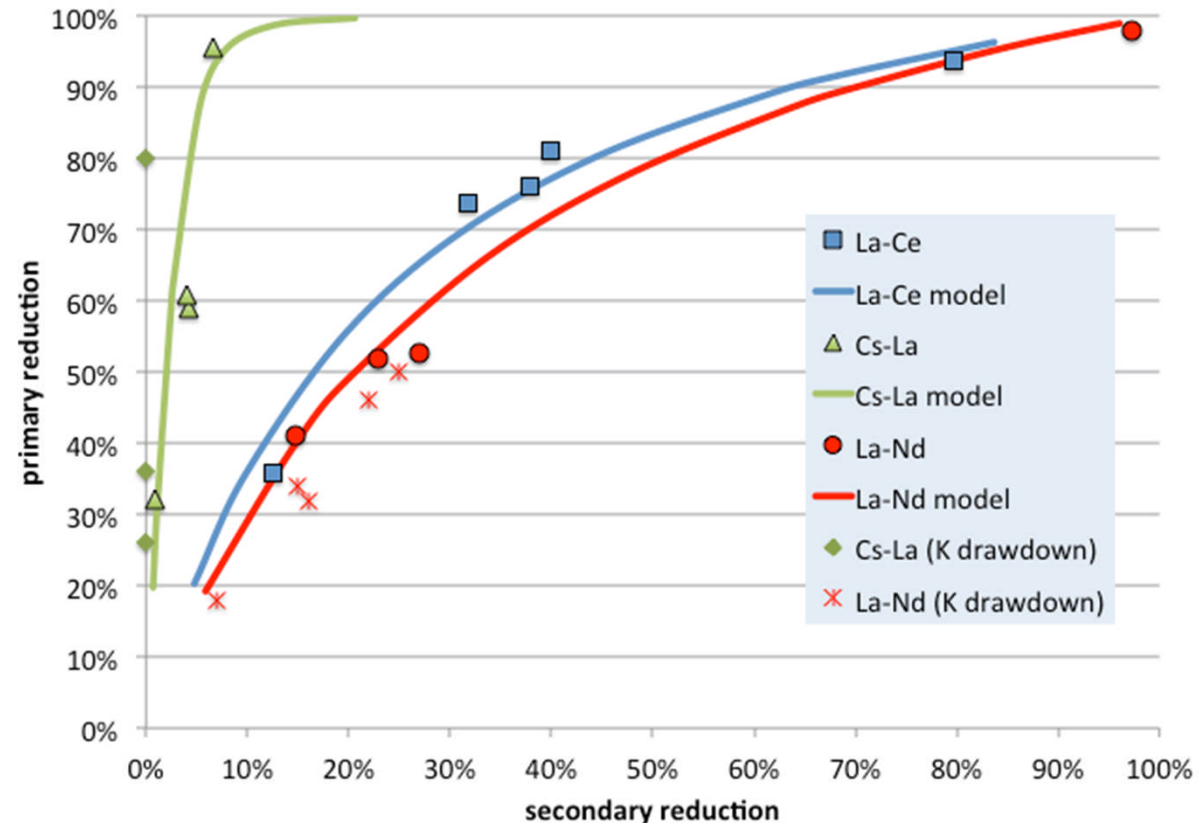
Selectivity for Reduction via Reaction with Metal

- **K drawdown experiments run by U.Idaho undergraduates.**

- Cs-La & La-Nd
- Higher T (593 C)
- Metal pieces added directly to the salt

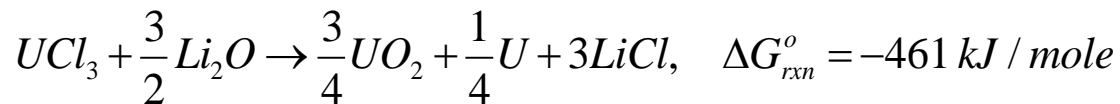
- **Based on limited data, it appears that the choice of reducing metal has little effect on selectivity.**

- Better selectivity of La in La-Cs
- Slightly lower selectivity for Nd in La-Nd



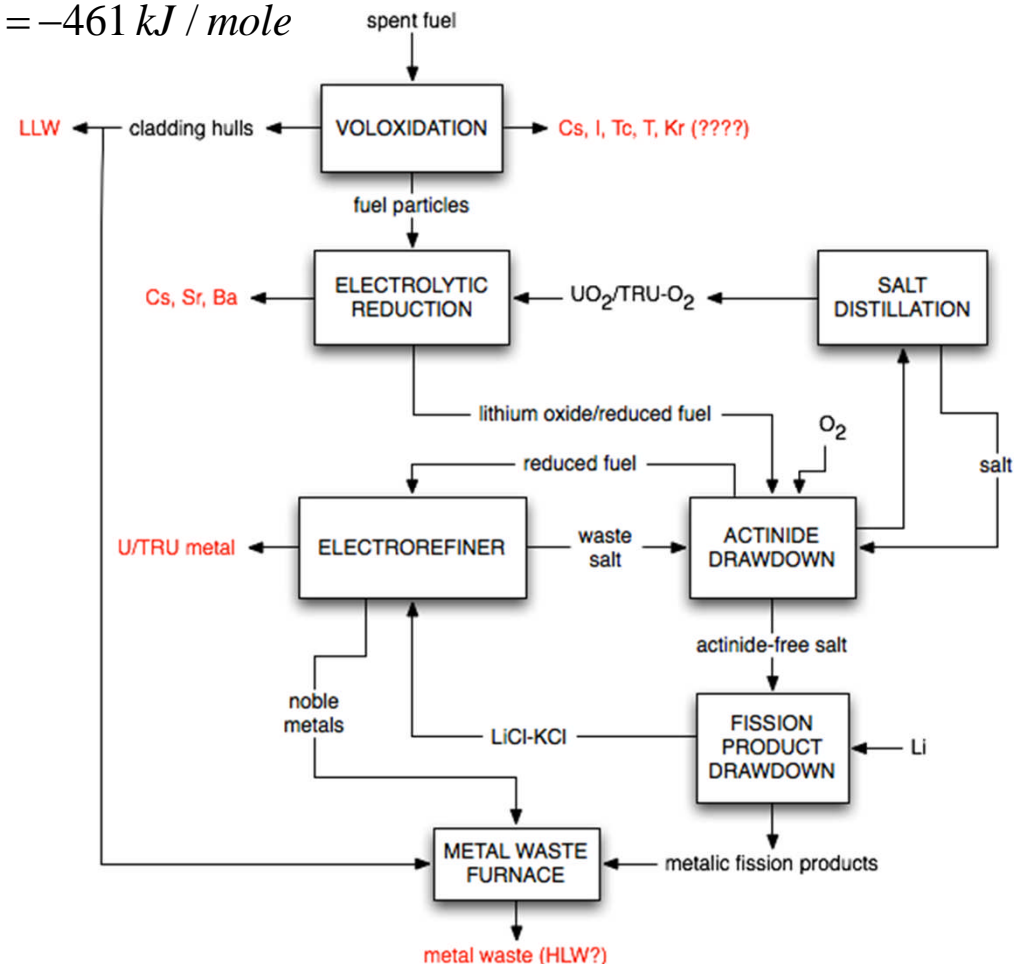


Reaction with Lithium Oxide



- Actinide oxychlorides appear to be thermodynamically favored
- Avoids potential corrosion from bubbling oxygen gas into molten salt
- Lithium oxide will normally carryover from oxide reduction process unless reduced fuel is subjected to distillation
- Unknowns
 - Whether oxides or oxychlorides form
 - Selectivity of actinide removal versus rare earth removal
 - Maximum extent of actinide removal without using excess Li_2O

Proposed Implementation Of Li_2O -Based Drawdown





U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Lithium Oxide Drawdown Tests with Rare Earth Chlorides

- Same experimental apparatus as used for Li drawdown tests

- Test conditions:

- T=500 C
- 8-10 hrs
- Salt stirred except for 10 minutes prior to taking sample
- “Mixed” refers to whether the Li_2O was held in a cup or mixed directly into the salt.

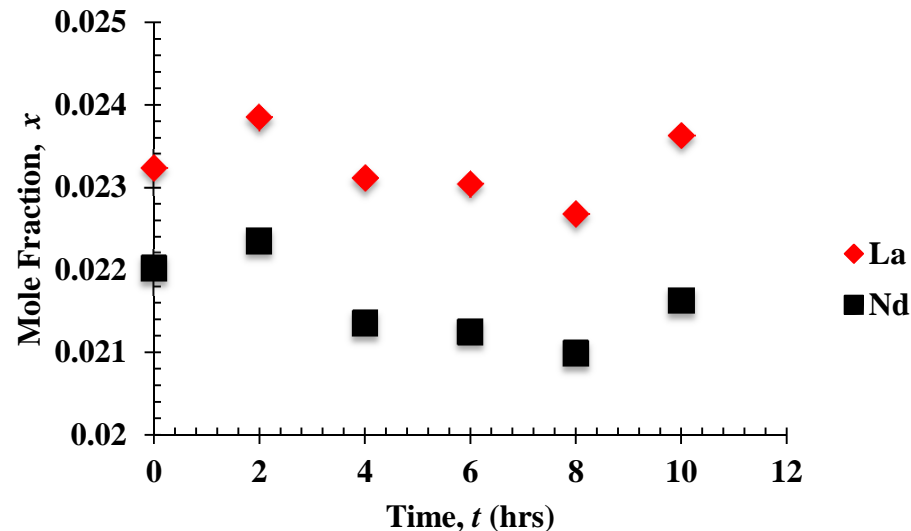
Test Matrix

<i>Test</i>	<i>LiCl-KCl (g)</i>	<i>NdCl₃ (g)</i>	<i>LaCl₃ (g)</i>	<i>Li₂O (g)</i>	<i>Time (hr)</i>	<i>Mixed?</i>
LO-1	30	3.4	3.4	0.14	10	No
LO-2	30	3.4	3.4	0.3	8	Yes
LO-3	30	3.4	3.4	0.9	8	Yes
LO-4a	30	3.4	3.4	0.60	10	No
LO-4b	30	3.4	3.4	0.60	10	Yes





Lithium Oxide Dissolution



- In LO-1 (results shown above), lithium oxide was loaded into sample cup and dipped into the salt (as shown on the right)
- Very little reaction of LaCl_3 or NdCl_3 was observed.
- Reaction rate appears to be limited by dissolution of Li_2O in the salt, since its solubility is only about 0.65 mol% in LiCl-KCl at 500 C. Total Li_2O immersed in the first experiment was equivalent to 0.89 mol% if completely dissolved in the salt.



Li_2O immersed into LO-4a

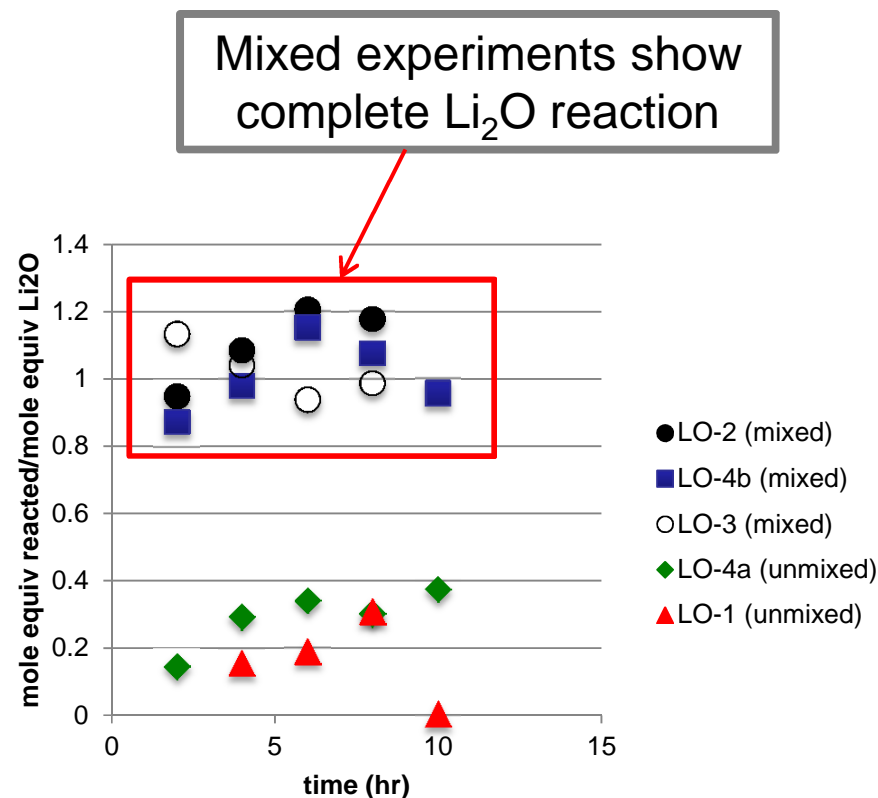
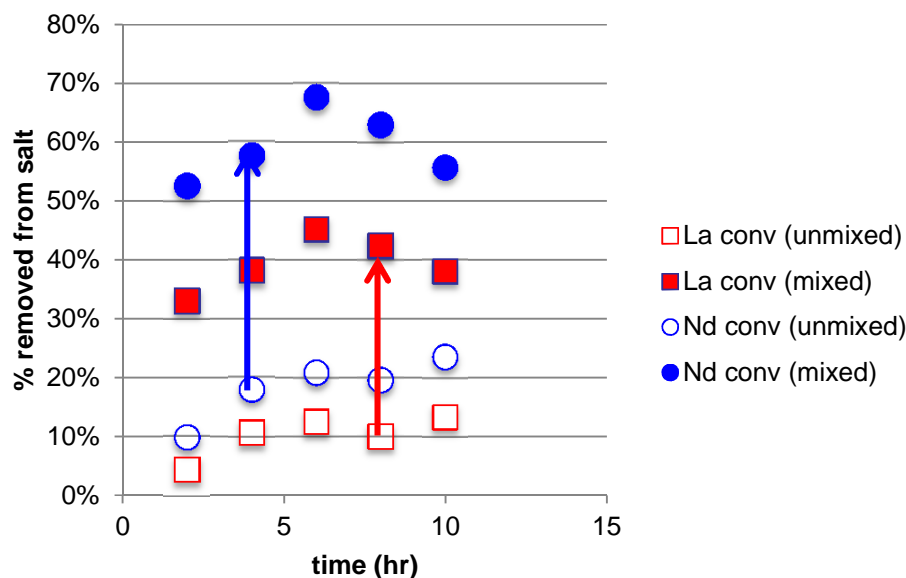


U.S. DEPARTMENT OF
ENERGY

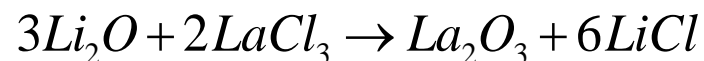
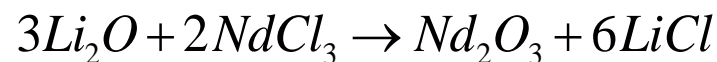
Nuclear Energy

Reducing Mass Transfer Resistance for Lithium Oxide Reaction

- In LO-2, LO-3, and LO-4b the Li_2O was added directly to the salt and mixed as a suspension.
- From results below, it can see that this facilitated the reaction.
- Extent of reaction is evidence of oxide formation.



Consistent Stoichiometry





Oxide/Oxychloride Precipitate

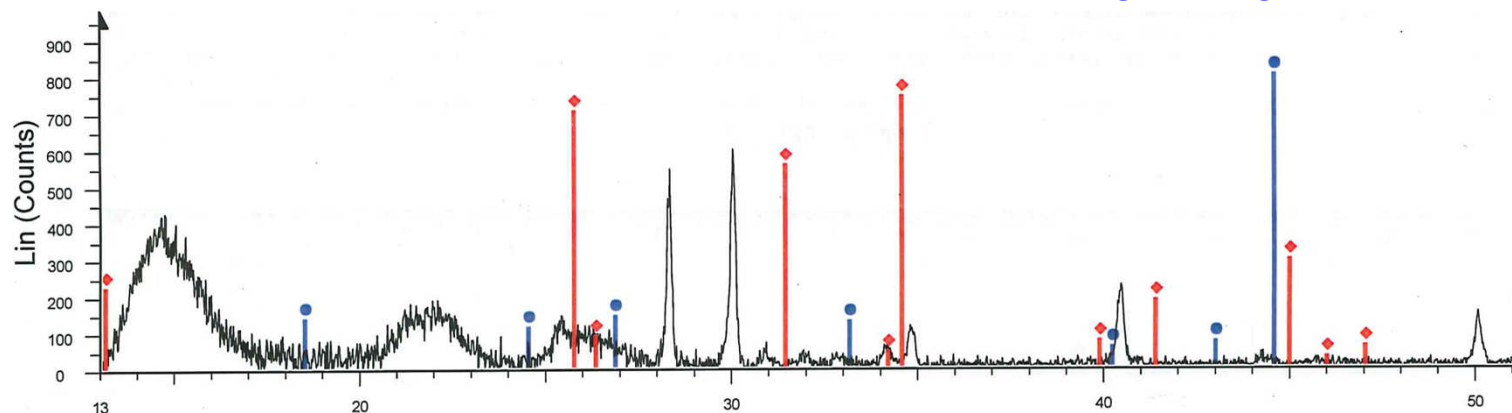
- Blue precipitate layer analyzed via ICP-MS and found to be concentrated in La and Nd.
- XRD pattern of blue region more consistent with oxide phases than oxychlorides.
- All results are consistent with Nd_2O_3 and La_2O_3 formation.

Fragment of Salt Showing
Precipitate Layer

white region high in Li/K



blue region high in RE

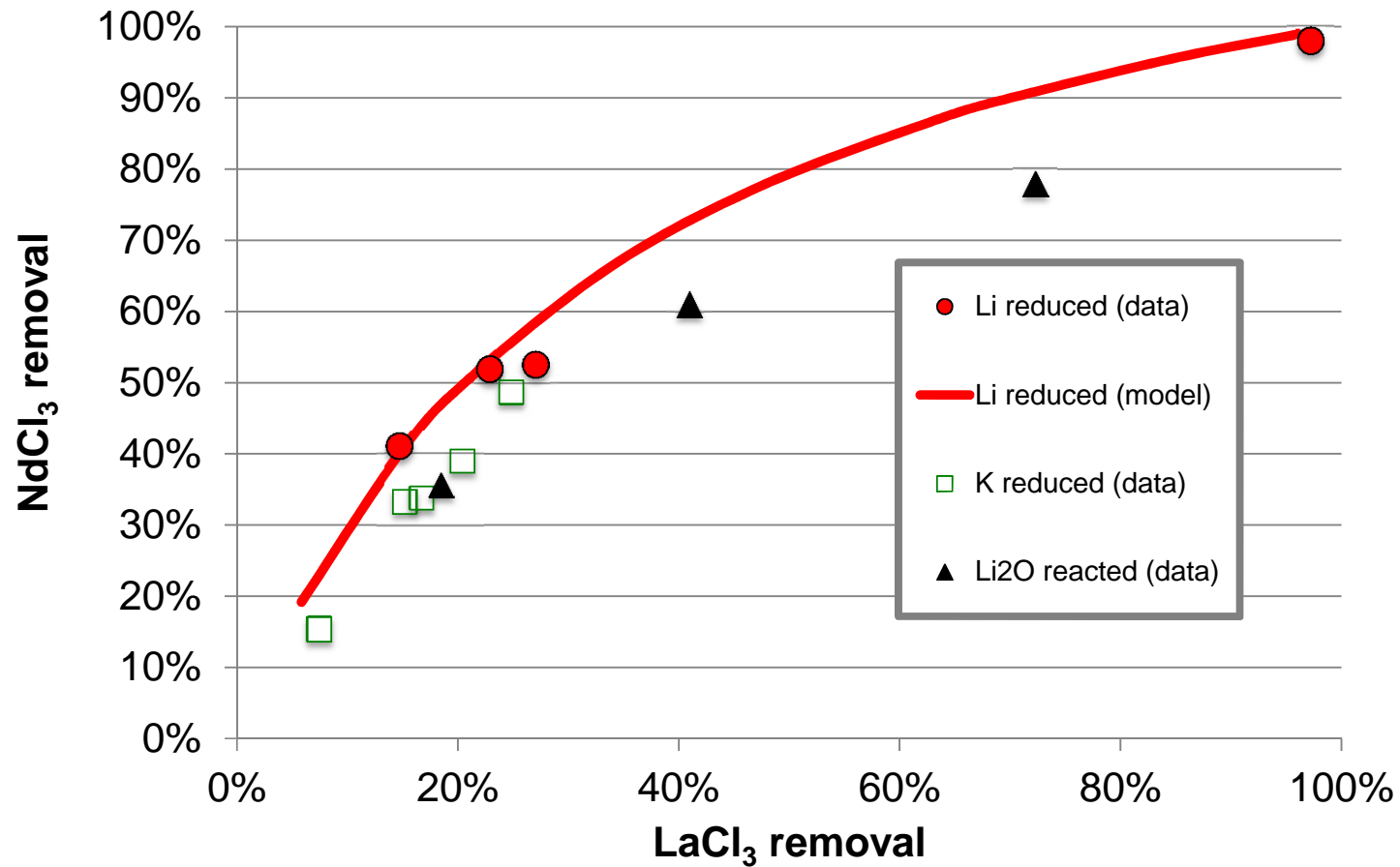




U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Selectivity Comparison for Metal and Oxide Precipitation Approaches





Conclusions

Nuclear Energy

- Reaction of metallic lithium with rare earth chlorides is fast and goes to completion in a very simple chemical reactor configuration.
- Potassium metal can likewise be used to reduce the rare earth chlorides.
- Reduction selectivity using lithium metal can be predicted with a model that is consistent with differences in free energy of formation of the rare earth chlorides.
- Limited lithium oxide solubility requires suspension of the powder in the molten salt to facilitate fast and complete reaction with rare earth chlorides.
- Nd and La chlorides primarily form oxides from reaction with lithium oxide at 500 C.
- All methods for removing rare earths have the drawback of low selectivity for specific species, but lithium metal reduction performs the best in this respect.
- While all of the examined approaches to drawdown are expected to be scaleable and economical, thermodynamic proximity between plutonium and rare earths is expected to require either some loss of plutonium into the waste stream or substantial carryover of rare earths into reduced product which would likely require post-processing to extract the rare earths.